Calculated and Experimental Vibrational Properties of P700 and the Iron Sulfur Cluster in Photosystem I

HARI LAMICHHANE, GARY HASTINGS, Georgia State University — Density functional theory (DFT) based vibrational frequency calculations of Fe$_4$S$_4$(SR)$_4$n$^-$ clusters show that the intense iron-sulfur stretching modes lie in the frequency region between 300-400 cm$^{-1}$. Among them the iron-sulfur ligand (Fe-S$_t$) stretching modes are more intense and $\sim$ 30 cm$^{-1}$ lower in frequency than the iron-sulfur body (Fe-S$_b$) stretching modes. Calculations in tetrahydrofuran (THF) show that all these iron-sulfur stretching modes of vibration downshift by $\sim$ 20 cm$^{-1}$ upon reduction of the molecule. On the other hand, we have not observed any intense bands from chlorophyll a in the frequency region 400 to 320 cm$^{-1}$ from the calculations. In an attempt to detect modes associated with iron sulfur clusters in PS I we have obtained light induced (P700$^+$- P700) FTIR difference spectra for PSI particles from S.6803 in the far infrared region. We observe difference bands at many frequencies in the 600-300 cm$^{-1}$ region. Based on our calculations and literature values we claim that the negative bands at 388 cm$^{-1}$ and 353 cm$^{-1}$ in the (P700$^+$- P700) FTIR difference spectra be assigned to Fe-S$_b$ and Fe-S$_t$ stretching modes of the ground state of the iron-sulfur cluster F$_B$. 

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Date submitted: 18 Aug 2009

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